REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
13-02-2015	Final Report	11-Feb-2013 - 10-Sep-2014

4. TITLE AND SUBTITLE
Final Report: Multicharged Ion Promoted Desorption (MIPD) of Reaction Co-Products

5a. CONTRACT NUMBER
W911NF-13-1-0042

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHORS
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
63759-MS-DRP.3

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
Multicharged ions (MCIs) produced in a new, electron beam ion trap (EBIT) based ion source, were investigated as a means of inducing athermal surface reactions for thin film processing. The specific surface systems investigated were highly oriented pyrolytic graphite (HOPG), nanodiamond (ND) and polycarbonate (PC). Beams of oxygen (Q=3+ and 5+) and argon (Q=1+, 4+, and 8+) ions were focused at normal incidence onto these target surfaces with fluences in the range of 10^12 – 10^13 particles per square centimeter. In-situ measurements of desorption and ex-situ measurements of surface modifications using mass spectrometry, Raman spectroscopy and XPS were made to

15. SUBJECT TERMS
multicharged ions, desorption, sputtering, surfaces

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Chad Sosolik
UU	UU	UU	UU		19b. TELEPHONE NUMBER: 864-656-0310

Report Title

Final Report: Multicharged Ion Promoted Desorption (MIPD) of Reaction Co-Products

ABSTRACT

Multicharged ions (MCIs) produced in a new, electron beam ion trap (EBIT) based ion source, were investigated as a means of inducing athermal surface reactions for thin film processing. The specific surface systems investigated were highly oriented pyrolytic graphite (HOPG), nanodiamond (ND) and polycarbonate (PC). Beams of oxygen (Q=3+ and 5+) and argon (Q=1+, 4+, and 8+) ions were focused at normal incidence onto these target surfaces with fluences in the range of 10^12 – 10^13 particles per square centimeter. In-situ measurements of desorption and ex-situ measurements of surface modifications using mass spectrometry, Raman spectroscopy and XPS were made to determine ion-induced effects. The primary ion-induced results were in the HOPG and PC systems, where the ion impacts led to structural changes that could be attributed to bond breaking (both HOPG and PC) and the formation of new solid phases (HOPG to diamond-like conversion). The structural changes observed in PC indicate a charge-dependent enhancement, and, consequently, dose-dependent effects with an onset at fluences three orders of magnitude below those required for singly charged ions surface processing of the same substrate.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
02/04/2015	2.00	Dhruva D. Kulkarni, Radhey E. Shyam, Daniel B. Cutshall, Daniel A. Field, James E. Harriss, William R. Harrell, Chad E. Sosolik. Tracking subsurface ion radiation damage with metal–oxide–semiconductor device encapsulation, Journal of Materials Research, (01 2015): 0. doi: 10.1557/jmr.2014.386
TOTAL:	**1**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
TOTAL:		

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper	
02/04/2015	1.00	R. Shyam, D. D. Kulkarni, D. A. Field, E. S. Srinadhu, D. B. Cutshall, W. R. Harrell, J. E. Harriss, C. E. Sosolik. First multicharged ion irradiation results from the CUEBIT facility at Clemson University, PROCEEDINGS OF THE XII INTERNATIONAL SYMPOSIUM ON ELECTRON BEAM ION SOURCES AND TRAPS. 18-MAY-14, East Lansing, Michigan. : ,

TOTAL: **1**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Daniel Field	1.00	
Dhruva Kulkarni	1.00	
FTE Equivalent:	**2.00**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Chad Sosolik	0.17	
FTE Equivalent:	**0.17**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
James Harriss	0.50
FTE Equivalent:	**0.50**
Total Number:	**1**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Scientific Progress

1. Statement of Problem Studied

The goal of this project was to investigate non-thermal chemistry at surfaces initiated by the interactions and/or impacts of multicharged ions (MCIs). This particular work was part of a larger DARPA effort to achieve low temperature thin film growth. Our initial work was focused on the chemistry of diamond growth, and, in particular, the removal of hydrogen from the growth surface as a means to open up new sites for carbon attachment and ultimately diamond film growth. Following Phase 1/Phase 2 efforts in this program, we shifted our focus to questions of adhesion for film growth and the ability of MCIs to change the hydrophobicity of thermoplastic polymers such as polycarbonate (PC).

2. Summary of Most Important Results

The results of this work are summarized below and organized around the two systems studied: carbon materials and polycarbonate.

a. Carbon materials

The carbon materials investigated were highly oriented pyrolytic graphite (HOPG), nanodiamond (ND) and diamond-like-carbon (DLC). The HOPG samples were acquired from SPI Supplies, the nanodiamond samples were obtained from sp3 Diamond Technologies, and the DLC was obtained from Southwest Research Institute.

HOPG

For the HOPG materials, the irradiations were carried out using beams of Carbon and Argon ions with nominal kinetic energies of 1.0 keV. All sample irradiations were made with the samples at normal incidence to the incoming beams and post-analysis of these samples was achieved using Raman spectroscopy. It should be noted that the initial goal of these experiments was to determine an energetic threshold for damage in the irradiated HOPG samples that could then be used as a starting point (in kinetic energy) for irradiations of diamond-like targets.

In Figure 1 are shown typical Raman spectra for these samples. Comparing the three spectra (one pristine and two irradiated samples) it is clear that irradiation at this kinetic energy leads to the formation of new features in the 1000-1500 cm^{-1} wavenumber range. For both the C^{4+} and Ar^{8+} irradiations a feature labeled "D" appears, while for the Ar^{8+} a feature labeled "T" also appears. The "D" peak represents the breathing modes of sp2 atoms in rings and is indicative of ion-induced disorder within the structure. The "T" peak arises due to C-C sp3 vibrations and is most typically associated with nano-crystalline diamond structures. Although charge states below Ar^{8+} were used, the "T" structure was not observed until this threshold charge state was reached. This result is consistent with prior measurements of irradiation of HOPG structures, where scanning tunneling spectroscopy (STS) studies indicated diamond-like structure formation at single impact sites for multiply charged ions. A direct comparison of our result to other ion irradiation studies which indicate large scale changes in HOPG structure as it transitions from nano-crystalline graphite to amorphous Carbon phases is not reasonable. This is because those studies show transformational onset at defect densities of 10^{22} vacancies/cm^3 whereas the highest

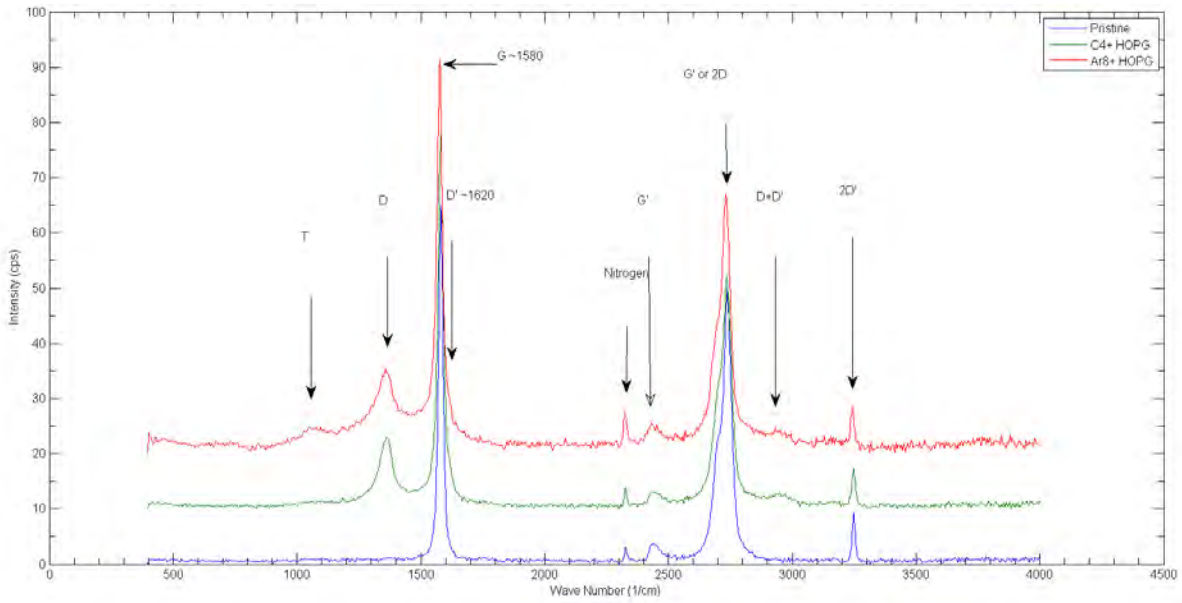


Figure 1: Raman spectroscopy scans of pristine HOPG and HOPG irradiated with C^{4+} and Ar^{8+} ions.

incident dose for our multiply charged beams was less than 10^{12} ions/cm^2, far below the number of impacts necessary to reach comparably high vacancy levels [1]. Therefore, it is most reasonable to conclude that at our dose levels and an incident energy of 1 keV, the ions are introducing highly localized surface disorder at far separated sites at the HOPG surface, which, in the case of the highest charged state (Ar^{8+}) is manifest as localized regions of nanocrystalline diamond [2].

Nanodiamond and Diamond-Like-Carbon

For the nanodiamond (ND) samples, the experimental measurements were limited to studies aimed at extracting yields for ion-induced desorption of hydrogen species from prepared/dosed samples. These measurements proved to be highly inconclusive due to an overall lack of sensitivity to these low mass species (either hydrogen or deuterium) within the experimental setup (a commercially available mass spectrometer from Stanford Research Systems). While the pursuit of these data led to the installation of a pulsing and timing system on our electron beam ion trap and beamline and a microchannel plate detector for improved sensitivity, this effort was suspended based on feedback from DARPA regarding our non-continuation in the overall LoCo effort.

For the diamond-like-carbon (DLC), a single sample was irradiated with a high dose of Ar^{8+} ions (2.5 x 10^{13} ions/cm^2) and then scanned using Raman spectroscopy at multiple, spatially-separated spots. These results, shown in Figure 2, indicated a spatially-varying signal for the DLC manifested as an overall loss in intensity in the spectrum in the most highly irradiated regions relative to pristine or unirradiated regions. This may be attributable to surface roughness in the highly irradiated regions. However, from our perspective, the most important part of this

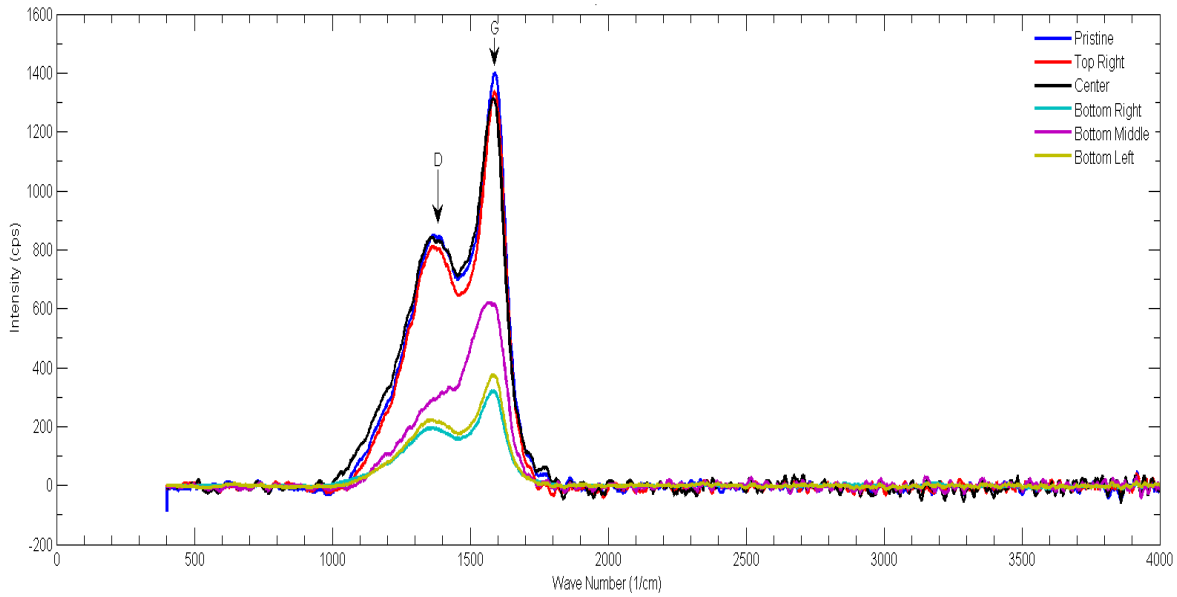


Figure 2: Raman spectroscopy scans of an Ar^{8+} irradiated DLC sample at several spatially-separated points. The overall variations in structure and intensity indicate both an ion impact effect and the convolution of this effect with the current density profile of the incident ion beam.

result was its indication that the effects of the multiply charged ions are extremely sensitive to the current density profile of the beam. Therefore, subsequent measurements with polycarbonate samples were preceded by a determination of the typical current density profile for the beams and a calibration of the alignment of this profile with positions near the center of irradiated samples.

b. Polycarbonate

Samples of polycarbonate (PC) were investigated under multiply charged ion irradiation as a transitional project following our release from our specific track on the Phase 2 team. The motivation for this work was the observation that the ultimate goal of the program has been to grow a film that would be adherent to a substrate that was constrained by its own low temperature properties. Therefore, a low temperature method for modifying the adhesion properties of such a substrate would be a desirable outcome. Prior measurements in the literature indicated that high dose singly charged ion irradiation was a method that could lead to surface structural changes that were beneficial to film adhesion [3,4]. In particular, changes in the hydrophobicity of a PC substrate were indicative of improved adhesion properties. For our setup, one standard method for testing hydrophobicity, the contact angle for a water droplet, was deemed infeasible given that our beam size (few mm) was comparable to or even smaller than the typical "test drop" size. Therefore, we designed a set of measurements that would utilize x-ray photoelectron spectroscopy (XPS) as a means to interrogate the ion-irradiated surface of a PC sample.

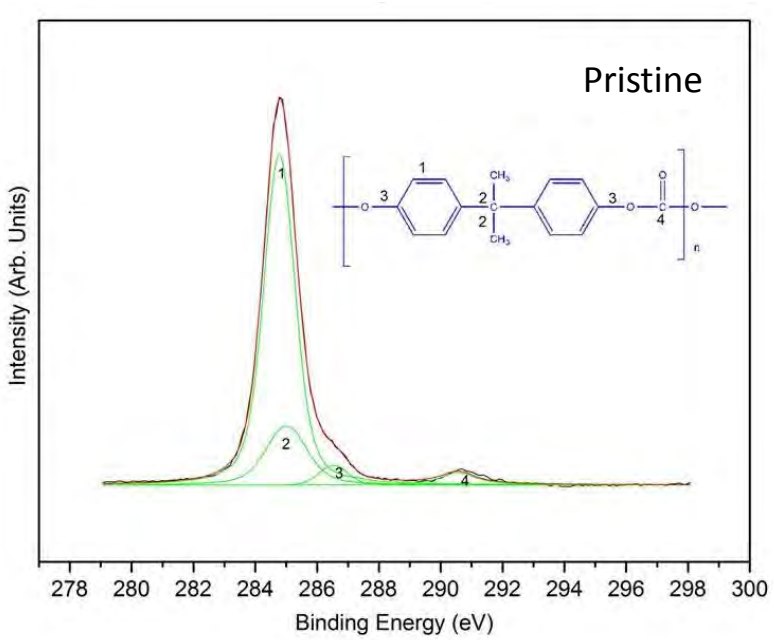
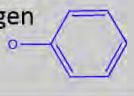
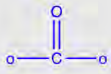


Figure 3: A representative XPS spectrum taken on a pristine, i.e. unirradiated, polycarbonate (PC) sample. The inset shows the basic PC structure and numbers 1-4 label the bond/peak assignments within that structure and the XPS spectrum.

In these measurements, a large PC sheet (300 mm x 1200 mm) was obtained from United States Plastic Corp. and diced into individual samples for irradiation by Oxygen and Argon ions. As in previous irradiation studies on carbon samples, the incident beam was held at normal incidence to the substrate. The incident dose range was 10^{12} to 10^{13} particles per cm^2 and the incident ion energy was held at 1 keV for all species and charge states. All XPS measurements were made using the cleanroom facilities at Georgia Tech University. A typical pristine C1S XPS spectrum on PC is shown in Figure 3. The primary peaks, labeled 1-4, correspond to the aromatic and aliphatic bond types shown in Table 1. For these data, we considered, that changes in the intensities of these peaks would correspond to changes in substrate hydrophobicity in the irradiated region probed. These peak intensity changes were tracked as a function of dose and for different ions and charge states.

TABLE 1

Chemical Composition/ Structure	No. of Carbon atoms	Intensity	Types of Bonds present
Aromatic 	10	HIGHEST (1)	Average Bond length is 1.5
Aliphatic 	3	(2)	2 (C-C) bonds
Aromatic Carbon bonded to Oxygen 	2	(3)	Aromatic (C-O)
CO_3 	1	LOWEST (4)	1 (C = O) 2 (C – O)

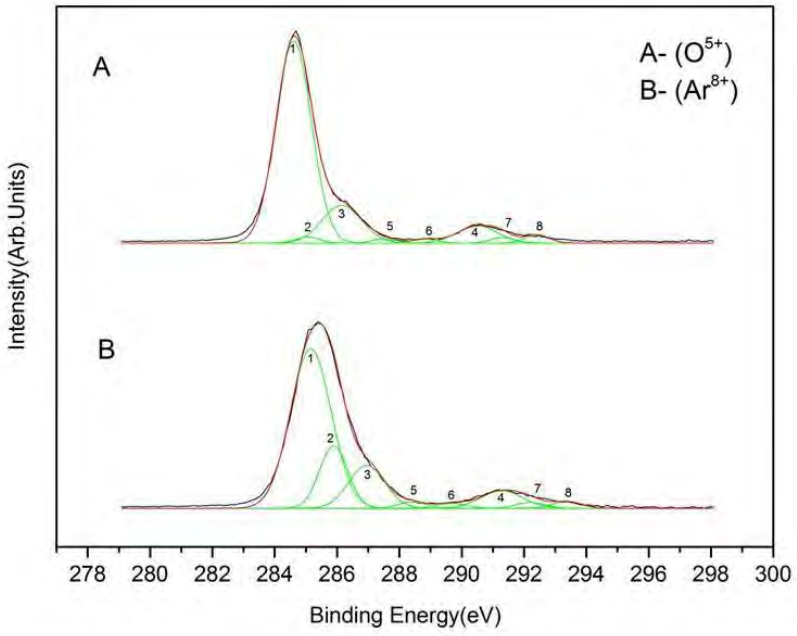


Figure 4: Representative XPS spectra taken on polycarbonate (PC) samples irradiated with O^{5+} and Ar^{8+} ions.

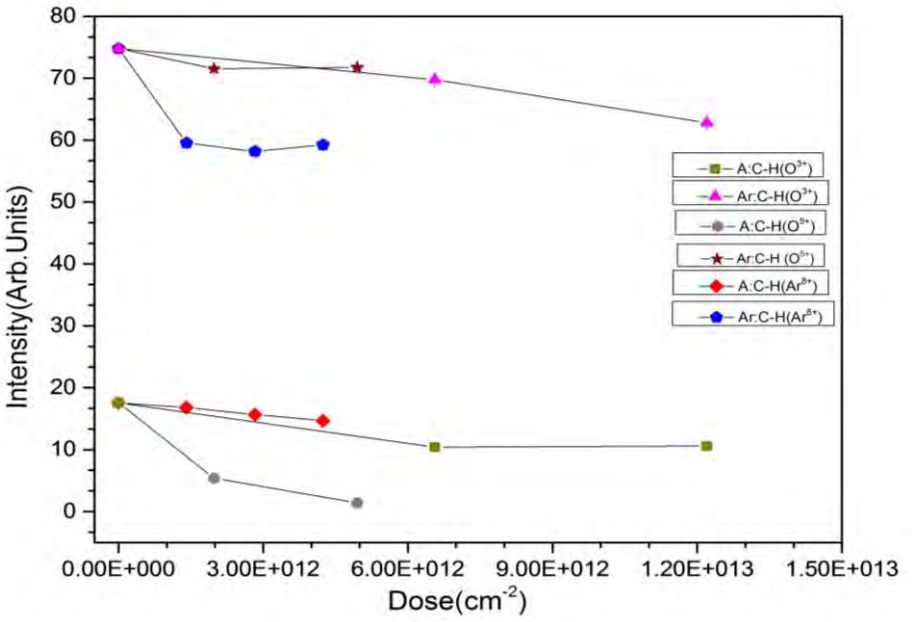


Figure 5: The change in intensity for C-C bonded species at a PC surface as extracted from XPS spectrum intensities, plotted with respect to the dose of incident O^{5+} and Ar^{8+} ions.

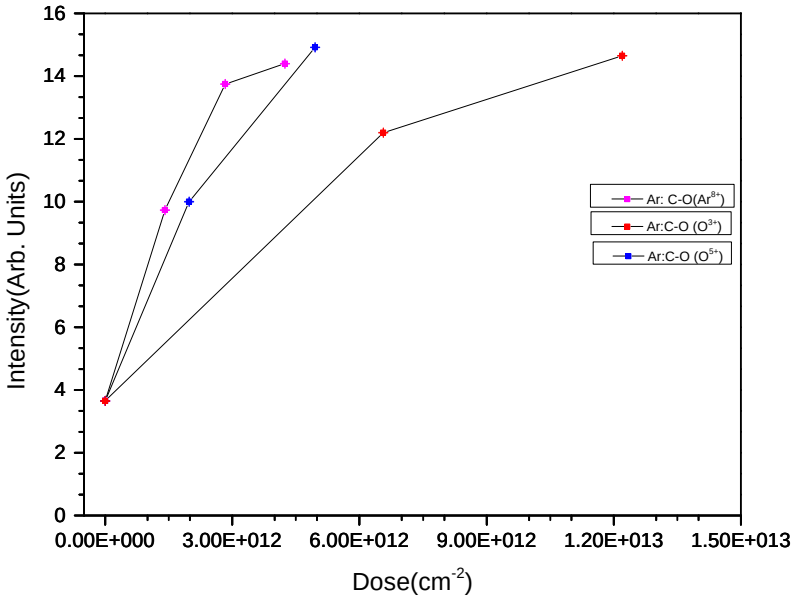


Figure 6: The change in intensity for C-O bonded species at a PC surface as extracted from XPS spectrum intensities, plotted with respect to the dose of incident O^{5+} and Ar^{8+} ions.

In Figure 4 are shown some typical XPS spectra for PC samples irradiated with O^{5+} and Ar^{8+} ions. A qualitative comparison to the pristine spectrum from Figure 3 makes it clear that in either of the irradiated cases, the ions have led to the significant changes in the relative intensities of peaks 1-3 as well as the introduction of new features (fit as peaks 5-8) into the spectrum. The shifts in the integrated intensity of these features as a function of the total ion dose are shown in Figures 5 and 6 for C-C bonds and C-O bonds, respectively. These changes, calibrated per incident ion at a fixed dose, are summarized in the histogram of Figure 7 and listed according to the potential energy of the three ion species used.

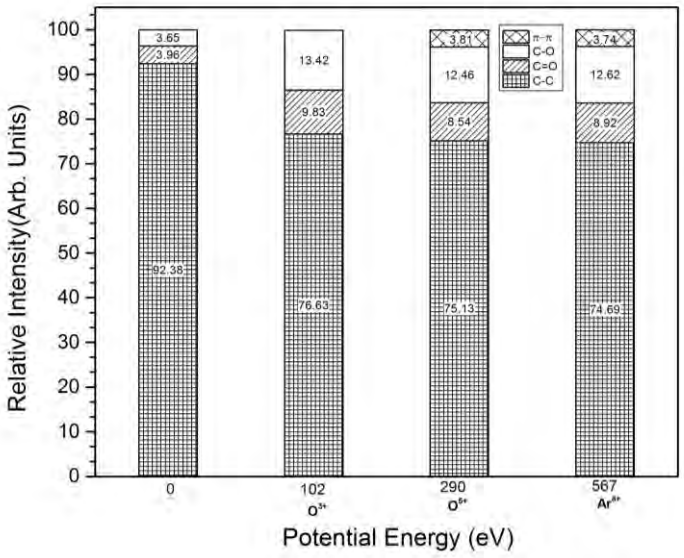


Figure 7: Histogram of the relative integrated intensities of the bond structures at a PC surface for pristine and irradiated samples. Intensities are extracted from XPS spectra, with the irradiated data representing the bond structures present after a fixed, standard dose of ions (~5 x 10^{12} cm^{-2}) was used for the three species/charge states investigated.

If these data are considered in terms of the histogram of Figure 7, we can conclude first that the results show that all of the multiply charged ion species used lead to surface bonding changes (per ion) that are relatively comparable. While this appears to be a somewhat inconclusive result in terms of specific multiply charged species, the overall data indicate a significant enhancement in the ability of all of the species to affect surface bonding. Specifically, the incident dose range used (10^{12} to 10^{13} ions/cm^2) is approximately three orders of magnitude below that required to achieve similar effects in singly charged ion irradiations. For these singly charged ions, this dose range (approximately 10^{16} ions/cm^2) is physically understandable as it corresponds roughly to one incident ion per surface atom needed to effect a change. Therefore, for multiply charged ions, the three order of magnitude drop in required dose points to a charge state mediated enhancement in the ability to break and/or change surface bonding characteristics in PC. The relatively flat dependence on ion charge state seen here could indicate that for these data we are

in a saturated regime for this enhancement, and further results across a wider charge state range would likely elucidate the full dependence on charge state (or ion potential energy).

3. Bibliography

[1] S. Prawer et al., “Raman spectroscopic investigation of ion-beam-irradiated glassy carbon”, Journal of Applied Physics 68, 2361 (1990).

[2] T. Meguro et al., “Creation of nanodiamonds by single impacts of highly charged ions upon graphite”, Applied Physics Letters 79, 3866(2001).

[3] S-K. Koh, S-K. Song, W-K. Choi, H-J. Jung, “Improved wettability of polycarbonate and adhesion with aluminum by Ar+ ion irradiation”, Journal of Materials Research 10, 2390(1995).

[4] W. Choi, S. Koh and H. Jung, “Surface chemical reaction between polycarbonate and kiloelectronvolt energy Ar+ ion in oxygen environment”, Journal of Vacuum Science and Technology A 14, 2366(1996).